

Optical, Thermal and Topological Characterization of Quaternary $\text{Se}_{65}\text{Ge}_{15}\text{Te}_{20-a}\text{Sb}_a$ Chalcogenide Glasses

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Abstract— *Se-Te based chalcogenide glasses have been found suitable for optical memory devices due to their distinct amorphous-to-crystalline transformation. In the present work alloys of $\text{Se}_{65}\text{Ge}_{15}\text{Te}_{20-a}\text{Sb}_a$ ($a = 3, 6, 9, 12, 15, 18$) glasses have been synthesized using melt quench technique. Author report investigations leading to optical, thermal and topological properties of these glasses by varying the concentrations of Te and Sb. Glass transition and crystallization kinetics of alloys have been investigated using differential thermal analysis at different heating rates (5, 10, 15, and 20 Kmin⁻¹). The results so obtained verify the usefulness of above composition.*

Keywords—*Thermal stability, activation energy, glass forming ability, optical constants.*

I. INTRODUCTION

It has now very well established that chalcogenide glasses are very promising materials due to their wide range of scientific applications. An increased interest in chalcogenide by various researchers is due to their applications in infrared optical fibre communication, environment and materials science [1–3]. Chalcogenide glasses are widely used in phase-change memories applications. The phase-change materials are designed with rapid inter conversion. These glasses are also very useful for rewritable optical recording due to their reversible switching behaviour between phases. As the amorphous state is meta-stable, it has the possibility to transform into more stable crystalline state [4, 5].

Chalcogenide glasses are more weakly bonded materials as compared to oxide glasses, resulting in the formation of both hetero-polar (e.g., Ge-Se) and homo-polar (e.g., Se-Se; Ge-Ge) bonds. Amorphous selenium is widely used as amorphous semiconductor, but holds various disadvantages like poor sensitivity and short life time [6]. These shortcomings may be improved by alloying the amorphous selenium with other materials such as Te, Bi, Ge, Sb, Sn etc. The binary

chalcogenide glasses, involving selenium, are reported to have several advantages over pure and amorphous selenium and also found more useful in practical applications [7]. For better applicability, these must be thermally stable as far as time and temperature during use are concerned.

In order to explore the technological applications of the material, we need to study its optical and thermal behaviour. In order to improve the properties of the Se-Ge glassy system various efforts have been made by various authors, and during this process elements such as Te, Sb, Sn, Pb have been incorporated in this system [8–10]. It is an established fact that Germanium strengthens the glass matrix by increasing the cross-linking in the network, which affects the thermal and optical properties. Antimony is a good suitable tailoring agent to tune the physical properties of a material for a particular technological application. Due to heavy atomic mass of Sb than Ge, there is red shift in the absorption edge and reduction in the intrinsic optical losses in Ge-Se bond matrices. The weaker bond strength of Se-Sb bonds and hindrance introduced by large size of Sb causes strain and weakens the glass matrix, which opens the possibility to reduce the gap between the melting and peak crystallization temperature and make its suitability for phase change material.

II. ALLOY PREPARATION

Chalcogenide glasses in bulk or their thin films were prepared using high purity elements (99.999 %). These materials were weighed in to quartz ampoules. After sealing the ampoules, under high vacuum conditions (10⁻⁵Torr), they were suspended in a vertical furnace at 900°C for 24 hours and also shaken vigorously for homogeneous mixing. The temperature was raised very slowly at a rate of 4 K/min. For making amorphous alloy the melt was rapidly quenched in ice-water mixture. The samples were then kept at room temperature in dark for about one month for attainment of thermodynamic equilibrium as stressed by Abkowitz in chalcogenide glasses

[11]. Amorphous nature of the samples was again ensured by the absence of any sharp peaks in the X-ray diffractograms. Then various crystallization studies were carried out along with optical studies.

III. RESULTS AND DISCUSSION

3.1 Transmission spectra

Transmission spectra $\text{Se}_{65}\text{Ge}_{15}\text{Te}_{20-a}\text{Sb}_a$ ($a = 10$) thin films shows that the transmission shifts towards longer wavelength with Sb addition to the ternary system. A red shift has been observed in interference free region of spectra shown in figure 1. In the region of weak and medium absorption where ($\alpha \neq 0$), the transmittance decreases mainly due to the effect of absorption coefficient (α) and the refractive index (n). In the region of strong absorption, the transmittance decreases drastically, due to almost exclusively the influence of α and n whose values can be estimated by extra plotting the values in other region.

3.2 Refractive index

The increase in refractive index has been explained using polarizability of atoms. The replacement of Te with Sb leads to a decrease in refractive index of the system [12]. The decrease in the value of k with addition of Sb content indicates that loss of light decreases due to scattering fig 2. A red shift evident from the Kramers–Kronig relation also supports the decreased refractive index [13,14].

The refractive index (n) and polarizability are linked by the relation given by Lorentz – Lorentz

$$\frac{n^2 - 1}{n^2 + 2} = \frac{1}{3\epsilon_0} \sum_i N_i \alpha_i$$

where n is the refractive index of alloy, α_i is the polarizability and ϵ_0 is the permittivity of the free space and N_i is the number of polarizable units per unit volume.

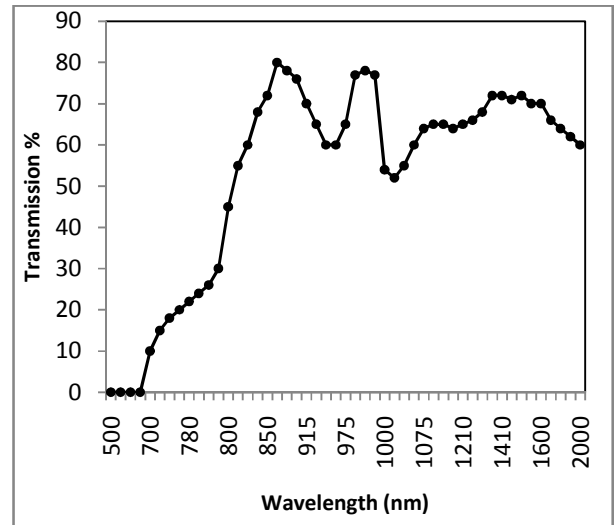


Fig. 1: Transmission curve

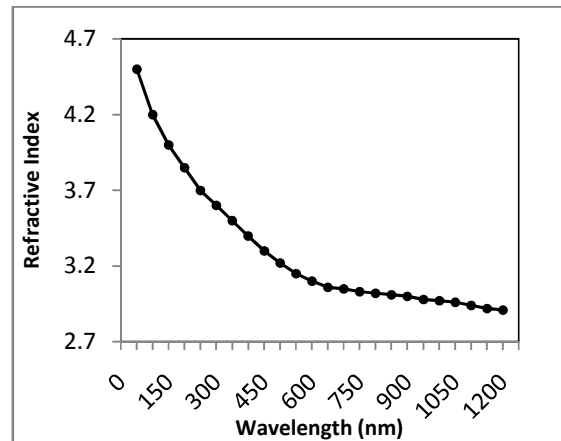
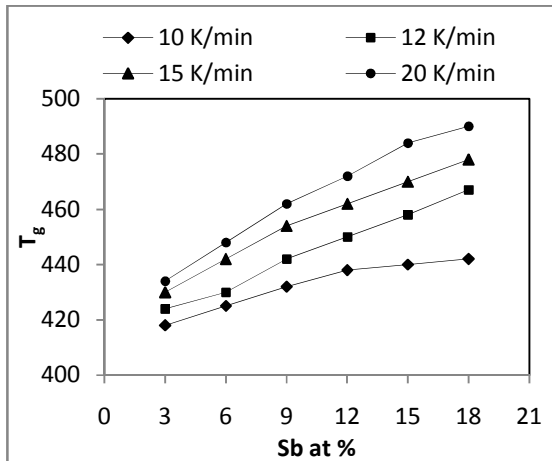


Fig. 2: Variation of Refractive Index with wavelength

3.3 Compositional and heating rate dependence of T_g and E_t

When the atomic percentage of Sb is increased in Se-Ge-Te-Sb glass system, Sb is expected to combine preferably with Se because the bond energy of Sb - Se (170.4 kJ/mol) is greater than that of Sb -Te (125.6 kJ/mol). This results in decreasing Se-Se bonds. The number of the Sb-Se bonds increases with increasing Sb content [7]. The variations of T_g as a function of Sb content in the Se-Ge-Te-Sb system have been shown in the following figure 3, it is clear that the value of T_g increases with the increase in heating rates, as well as with increases in Sb content. This explains the increase in T_g with the increase in Sb content due to the formation of large number of hetero-polar Sb -Se bonds and decrease in homo-polar Se-Se, Te-Te and Te-Se bonds [11].

Fig. 3: Variation of T_g versus Sb content

The dependence of T_g on the heating rate β has been calculated by the empirical relationship of the form.

$$T_g = A + B \log \beta$$

The values of β are found to be different for different glass compositions, indicating that Se-Ge-Te-Sb alloy undergoes structural changes for different Sb concentration, because values of β is an indication of the response of the configurationally changes within the glass transition region.[15]

The crystallization process involves two types of activation energies: activation energy for nucleation and activation energy of crystal growth. Further the literature study shows that the activation energy of crystal growth may be taken as equal to the activation energy of the whole crystallization E_c . The activation energy of crystallization has been determined by using the established model given by Kissinger

$$\ln \left(\frac{T_g^2}{\beta} \right) + \text{const} = \frac{E_t}{T_g} \quad (1)$$

The Kissinger equation can approximately be written by the form

$$\ln \beta = -\frac{E_t}{KT_g} + \text{const} \quad (2)$$

The plot of $\ln \beta$ for relations (1 & 2) has been depicted in fig 4.

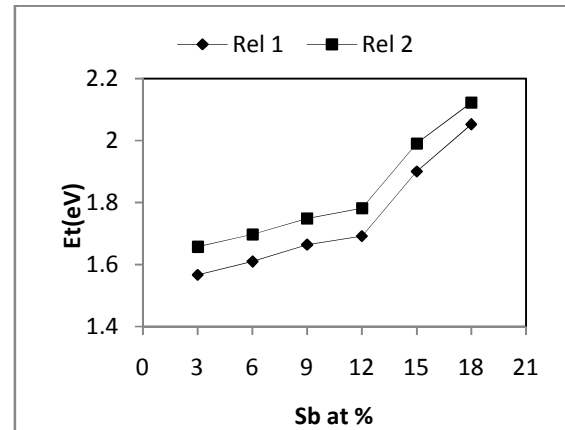


Fig. 4: Variation of activation energy with Sb content

Here, the activation energy is found to increase because of cross-linking in glass matrix. Further as the Sb content increases in the glassy matrix, it ruptures the Se polymeric rings and Se-Se bonds got replaced by Sb-Se bonds, so the activation energy increases.

3.4 Cohesive Energy

The stabilization energy of an infinitely large cluster of material per atom, also known as the cohesive energy of the system, was calculated using a well known approach, known as the Chemical Bond Approach (CBA). According to Chemical Bond Approach, the atoms combine more favourably with atoms of various kinds, until all the available valences of the atom are completely filled. The hetero-polar bond energies can be calculated by the following relation

$$E(A-B) = [E(A-A) + E(B-B)]^{0.5} + 30(X_A - X_B)^2$$

where $E(A-A)$ and $E(B-B)$ are the homo-polar bond energies while χ_A and χ_B are corresponding electro negativities [16].

The cohesive energy may be calculated by using the following relation

$$CE = \sum C_i E_i$$

here C_i denotes distribution of chemical bonds and E_i denotes energy associated with the corresponding bonds. From fig 4, it is evident that cohesive energy decreases with increase in Sb content from 3 to 18 at %. The selenium atoms are strongly bonded to germanium atoms and fill all the available valences of the Te and Sb atoms respectively. But, even then, there are some unsaturated Se atoms which appear as excess Se-Se bonds in the system.

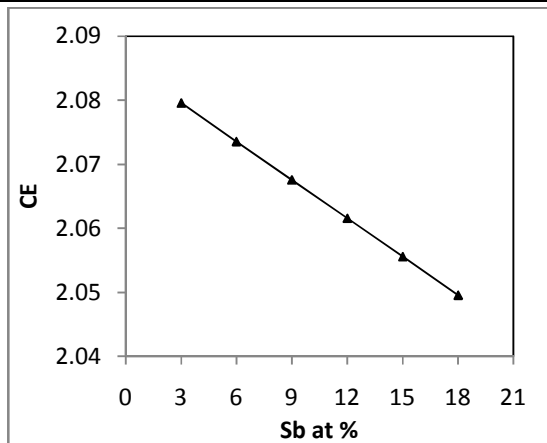


Fig. 5: Variation of cohesive energy with Sb content

Te decreases (2.131 eV Bond Energy) with increase in Sb content (1.97 eV Bond Energy), therefore, Se–Te bonds concentration also decreases, resulting in decrease of overall bond energy of the system and hence the value of cohesive energy. The value of cohesive energy decreases from 2.080 to 2.050 with increase in concentration of Sb from 3 to 18 at % as shown in fig. 5.

3.5 Ionic Character of Covalent Bond

It is now a well established fact that all bonds are absolutely covalent for coordination number $Z = 2.4$ [17, 18]. But for any value of Z other than $Z = 2.4$, the covalent bonds have some ionic character in order to confirm the nature of molecule as polar. The ionicity describes the tendency towards ordering due to non-directional character. The ionicity of a bond can be calculated by using the famous Pauling formula.

$$\text{Percentage of ionic character} = 1 - e^{0.25(\chi_A - \chi_B)^2}$$

where $(\chi_A - \chi_B)$ is denoting the difference in electro negativities of atoms A and B. There must be a direct connection between glass formations and bond strength [19]. The glass forming tendency used to be increased as a result of high value of bond strength. Since chalcogenide glasses are formed by materials such as S, Se, Ge, Te etc., which have predominantly covalent bonds, the degree of covalence in the bond of amorphous glass may be calculated by using the Pauling relationship as

$$\text{Amount of covalent character} = e^{0.25(\chi_A - \chi_B)^2}$$

Higher the covalent character, higher will be the tendency of glass formation; hence the elements with more than 90% covalent character are more predominantly form the glasses.

3.6 Average Coordination Number

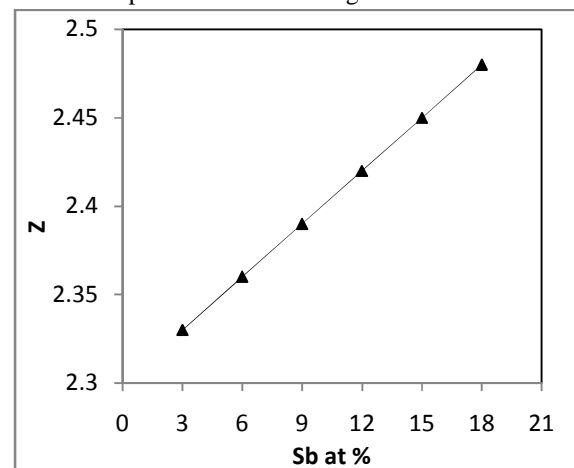
As per predictions as reported by Phillips [17], when the number of degrees of freedom exactly equals the number of constraints, the tendency of glass formation would be maximum. For the composition $\text{Se}_{65}\text{Ge}_{15}\text{Te}_{20-a}\text{Sb}_a$ ($a = 3, 6, 9, 12, 15, 18$), the average coordination number (Z) was calculated by using the standard method [18]

$$Z = \frac{wN_{\text{Se}} + xN_{\text{Ge}} + yN_{\text{Te}} + zN_{\text{Sb}}}{w + x + y + z}$$

where w, x, y, z and d are the at. % of Se, Ge, Te and Sb respectively and $N_{\text{Se}}(2), N_{\text{Ge}}(4), N_{\text{Te}}(2)$ and $N_{\text{Sb}}(3)$ are their respective coordination number. The variation of average coordination number with Sb contents is illustrated in fig. 6, from where it is clear that values of Z increase from 2.33 to 2.48 with increase in concentration of Sb from 3 to 18 at %.

3.7 Deviation From Stoichiometry Of Composition

The parameter R is generally used to determine the deviation from stoichiometry [20]. It is expressed by the ratio of covalent bond possibilities of chalcogen

Fig.6: Variation of Z with Sb content

atoms to that of non-chalcogen atoms. For $\text{Se}_{65}\text{Ge}_{15}\text{Te}_{20-a}\text{Sb}_a$ ($a = 3, 6, 9, 12, 15, 18$) system, the parameter R is given by [19, 20].

$$R = \frac{wN_{\text{Se}} + yN_{\text{Te}}}{xN_{\text{Ge}} + zN_{\text{Sb}}}$$

where w, x, y, z are atomic fractions of Se, Ge, Te, and Sb respectively. The threshold at $R=1$ (the point of existence of only heteropolar bonds) marks the minimum selenium content at which a chemically ordered network is possible without metal–metal bond formation. For $R>1$, the system is chalcogen rich and for $R<1$, the system is chalcogen poor.

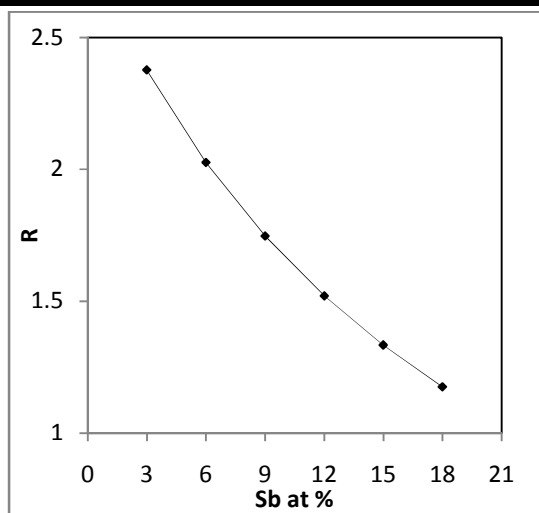


Fig. 7: Variation of R with Sb content

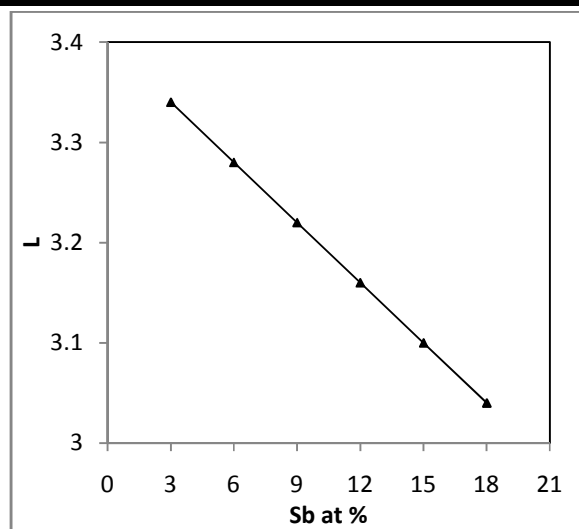


Fig. 8: Variation of Lone pair with Sb content

For quaternary chalcogenide $\text{Se}_{65}\text{Ge}_{15}\text{Te}_{20-a}\text{Sb}_a$ ($a = 3, 6, 9, 12, 15, 18$ at.%) the variation of stoichiometry with Sb contents is depicted in fig. 7.

It is clear from fig. 7 that parameter R decreases 2.38 to 1.18 with increase in concentration of Sb from 3 to 18 at. %, which clearly shows that our system is chalcogen rich, however, turning towards less chalcogen rich with the increase in content of Sb in the system, but still it is well within limits of being chalcogen poor. The high energy lone-pair electrons lead to qualitative different electronic densities of state due to chalcogen rich nature of the selected material.

3.8 Lone-pair

When the central atom is surrounded by one or more hybrid orbital containing lone pair of electrons in the valence shell, the geometry of the molecule is distorted to some extent. Since the lone-pair occupies more space around the central atom it can interact more and therefore it will repel the electron pairs in the neighbouring orbital's more strongly, whereas the repulsive interaction between the two bond pairs will be less [19,21]. This can be summarized as below.

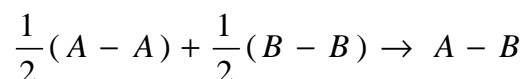
Lone-pair–Lone-pair repulsion > Lone-pair–bond-pair repulsion > bond-pair–bond-pair repulsion.

$$L = V - Z$$

The variation of lone pairs with Sb contents is shown in fig 8 which shows that the values of lone pair decrease from 3.34 to 3.04 with increase in concentration of Sb from 3 to 18 at. %.

3.9 Electronegativity

Electronegativity was defined by Pauling [19] as the power of an atom in a molecule to attract electrons to it self. Electronegativity of a composition may also be defined as the geometric mean of all the constituents required for forming a compound. In the present case, the presence of Sb makes the alloy typically ionic in character. Electronegativity was calculated from thermo dynamical data of different element and samples. Pauling considered that in a reaction of the type



The bond dissociation energy of (A – B) is higher than the mean of the bond dissociation energy of (A – A) and (B – B) bonds and their difference (Δ) is related to the difference of the Electronegativity of A and B according to the following empirical equation:

$$\Delta = E_{A-B} - \frac{1}{2}(E_{A-A} + E_{B-B}) = 23(X^A - X^B)^2$$

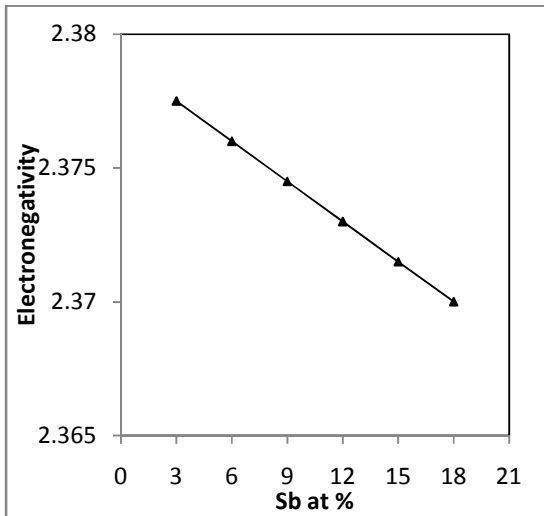


Fig. 9: Variation of electronegativity with Sb content

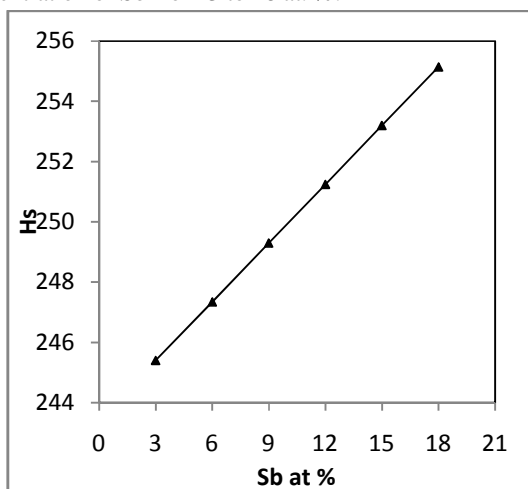
Where E_{A-B} , E_{A-A} and E_{B-B} represent the bond dissociation energy of A-B, A-A and B-B bonds respectively and χ_A and χ_B denotes the Electronegativity of A and B respectively. The values of electro negativity were found to be decreasing from 2.378 to 2.370 with increase in concentration of Sb from 3 to 18 at. % (Fig. 9).

3.10 Average Heat of Atomization

The average heat of atomization, H_s , may be defined and calculated as a direct measure of cohesive energy, for the present quaternary system $Se_{65}Ge_{15}Te_{20-a}Sb_a$ [22].

$$H_s = \frac{wH_s^{Se} + xH_s^{Ge} + yH_s^{Sb} + zH_s^{Te}}{w + x + y + z}$$

From figure 10 the values of H_s were found to be increasing from 245.39 KJ/mole to 255.14 KJ/mole with increase in concentration of Sb from 3 to 18 at. %.

Fig. 10: Variation of H_s with Sb content

3.11 Theoretical Band Gap

It is now an established fact that the values of band gap reflect the bond strength of the system. As discussed above about increase in values of H_s , if we divide it by Z , then average single bond energy (H_s/z), which specifies the bond strength, decreases with an increase in the Sb content from 3 to 18 at. % . Then the bond strength of the system also decreases. The following Shimakawa's relation has been used here to calculate the band gap values [23],

$$E_g = WE_g(Se) + XE_g(Ge) + YE_g(Te) + ZE_g(Sb)$$

where W, X, Y, Z are the volume fractions of Se, Ge, Te and Sb, respectively, while $E_g(Se) = 1.95$, $E_g(Ge) = 0.95$ eV, $E_g(Te) = 0.33$ eV and $E_g(Sb) = 0.101$ eV, are the energy gaps of corresponding element. The variations of E_g with increase in content of Sb are sketched in figure 11, which shows a decrease in the values of E_g from 1.429 to 1.413 with increase in concentration of Sb from 3 to 18 at. %.

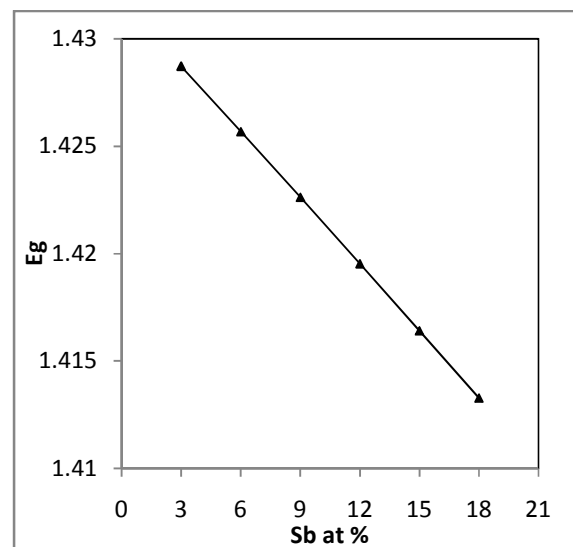


Fig. 11: Variation of band gap with Sb content

IV. CONCLUSIONS

A systematic investigation of the sample for different composition reveals that the energy band gap is found to be decreased with Sb% which is useful for the phase change memory. Study of $(\alpha\hbar\omega)^{1/2}$ versus $\hbar\omega$ plot and Reflection curve can be used in optical communication. Crystallization kinetics of $Se_{65}Ge_{15}Te_{20-a}Sb_a$ glass system reveals a heating rate dependence of T_g . The glass transition temperature T_g is found to increase with the increase in heating rates as well as increase in Sb at. %. The slight increase in T_g observed, with the variation of Sb content from 3% to 18%, is probably

due to the increase in mean molecular weight of the glasses with increasing Sb content.

The values of activation energies for glass transition E_t were found to increase with increase in Sb content. The values of activation energies, using two different methods, are in good agreement with each other. So it can be concluded that any of these two methods can be used to calculate glass transition activation energy. Therefore the thermal stability of these glasses is also found in good command to form the glasses with ease. All other physical parameters are also found to be varying linearly. It is concluded that the glasses with higher Sb content are easy to form compared to those with lower Sb content.

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